PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Production of Fibrous Materials

We, MONSANTO CHEMICALS LIMITED, a British Company of Monsanto House, 10—18 Victoria Street, London, S.W.1. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel processs for the production of fibrous materials.

It has been proposed to subject orientated thermoplastic materials to forces such that they are split up into fibrous structures, and two particularly useful processes of this kind are described in British Patent Specification Nos. 48527/64 (Serial No. 1114151) (cognated with 29324/64) and 48726/64 (Serial No. 1131282) (cognated with 43936/64).

British Patent Specification No. 48527/64 (Serial No. 1114151) (cognated with 29324/64) describes a process for the production of a novel fibre assembly which comprises drawing an extruded foamed thermoplastic material so that it becomes orientated essentially in one direction and subjecting the drawn foamed material to forces such that the walls of the foam are broken down and converted into a three-dimensional structure of interconnected fibre elements. British Patent Specification No. 48726/64 (Serial No. 1131282) (cognated with 43936/64) describes a process for the production of a novel textile yarn which comprises drawing a strand or ribbon of an extruded foamed thermoplastic material so that it becomes orientated essentially in the direction of extrusion and subjecting the drawn foamed material to forces such that the walls of the foam are broken down and converted into a three-dimensional structure of interconnected fibre elements.

We denote the process of breaking down the drawn material into a fibrous structure by the term "fibrillation". The specifications referred to above state that fibrillation can be effected by means of jets of air, but it has now been found that a turbulent stream of fluid provides a particularly useful means of fibrillating a drawn thermoplastic material.

The process of the invention is accordingly one for the production of a fibrous material which comprises drawing an extruded foamed thermoplastic material so that it becomes orientated essentially in one direction, and subjecting the drawn foamed material to the action of a turbulent stream of fluid so that the walls of the foam are broken down and converted into a fibrous material.

The material is broken down by a turbulent, as opposed to streamline, stream of fluid, and this causes the drawn thermoplastic material to vibrate within the stream of fluid so that fibrillation occurs. Vibration normally takes place at audio-frequencies, although ultrasonic and subsonic frequencies are very often also present, and the nature of this audible vibration has been found to provide an experienced operator with a useful check that proper fibrillation is taking place. The speed of the fluid stream needs to be sufficient to ensure the production of the required turbulence, but since this depends on the precise design of the apparatus employed it is not practical or necessary to lay down a definite rule on this point. Turbulence can for instance be produced or increased by placing a vibrating reed or other obstruction in the stream of fluid, and as will be explained the material to be fibrillated can itself constitute such an obstruction. Normally for any particular case a threshold of speed is found above which turbulent flow and fibrillation occur, and for each case it is a matter of simple experiment to determine the level of this threshold and ensure that it is exceeded and the necesssary

turbulence is produced. In general the fibrillation proceeds to a greater extent when the speed (and hence the degree of turbulence) is increased, and the extent of fibrillation desired consequently determines the most useful speed for the particular case under consideration. Very often it is found that there is a maximum degree of fibrillation that is not exceeded even when the fluid speed is considerably greater than that corresponding to this maximum. Subsonic velocities are usually preferable because supersonic ones are normally unnecessary and impose the need for expensive equipment, and it is for example rare for speeds greater than 20 feet per second to be needed.

The fluid can be a gas or a liquid, but it is preferably a gas, especially one that is inert to the thermoplastic material. Air is normally the preferred gas, although other gases such as for example nitrogen, carbon dioxide, argon or helium can be used if desired. Small particles of an abrasive material such as for example carborundum can be entrained in the stream of fluid if desired to assist in breaking down the foamed material into a fibrous structure. When a liquid is used, it is of course a non-solvent for the foamed material, although liquids which have a partial swelling action on the foamed material can be used. Examples of suitable liquids are water, acetone, methyl alcohol, ethyl alcohol, benzene, toluene and xylene.

In general in the instance of thermoplastic resins the temperature at which the fibrillation is carried out is room temperature, 20°C., or somewhat higher perhaps up to 30°C. In the instance of certain specific thermoplastic resins (particularly those which possess a degree of elasticity and are therefore relatively tough), and of elastomeric material in general, the temperature used is normally lower than room temperature, for instance 5°C. or 0°C. or even lower.

Fibrous materials in a wide range of forms can be produced by the process of the invention, depending partly on the foamed starting material but more especially on the conditions, such as type of apparatus, fluid speed and so on, under which the fibrillation is carried out. For example the process can lead to the production of a fibre assembly as described in British Patent Specification No. 48527/64 (Serial No. 1114151) (cognated with 29324/64), or to a yarn as described in British Patent Specification No. 48726/64 (Serial No. 1131282) (cognated with 43936/64), or if carried further can be used to produce discrete fibres. The process is particularly applicable to the production of textile yarns.

The thermoplastic material is one capable of being formed into an extruded foam; it is in practice usually a synthetic material, and one that is fibre-forming. Excellent results are obtained with a thermoplastic synthetic material, for example a polymer or copolymer obtained by polymerisation (which includes copolymerisation) of an ethylenically unsaturated monomer. Such a monomer can be an ethylenically unsaturated hydrocarbon, but it can be for instance a nitrile, such as acrylonitrile or methacrylonitrile; vinyl or vinylidene chloride; a vinyl ester, such as vinyl acetate, or an acrylate ester, such as ethyl acrylate or methyl methacrylate. Where the monomer is a hydrocarbon this can be a monoolefin, a diene, or a vinyl-substituted benzene, for instance ethylene, propylene, a butylene, a pentene or a hexene; butadiene; or styrene or α-methylstyrene. For example the polymer can be polyethylene (low density or more preferably high density material), crystalline polypropylene, or polystyrene or a toughened polystyrene. A copolymer can in general be for instance one involving two or more (such as three) of any of the monomers referred to above. A comonomer can for instance be one of a type which will impart a degree of flame-retardance to the copolymer, and an example of such a substance is a vinyl halide, such as vinyl chloride, vinyl bromide or vinylidene chloride. Examples of other comonomers are vinylpyrrolidone and a vinylpyridine such as methylvinylpyridine. A copolymer can for example be one derived from two hydrocarbon monomers, such as an ethylene-propylene or styrene-butadiene copolymer; or a hydrocarbon and a different type of monomer, such as an ethylene-vinyl acetate copolymer; or a copolymer derived from dissimilar monomers such as for example acrylonitrile and a minor proportion of vinyl acetate. The thermoplastic material can also consist of a mixture of two or more polymers or copolymers; it can for example comprise a mixture of a copolymer of acrylonitrile with a minor amount of vinyl acetate (in the region for instance of 10% by weight) and polyvinyl chloride; or a mixture of an acrylonitrile-vinyl acetate copolymer and a copolymer of acrylonitrile with methylvinylpyridine. Preferably the polymer is a thermoplastic resin material, but it can be an elastomeric material, for instance a copolymer derived from sufficient of a diene monomer (such as butadiene) to impart some degree of elastomeric properties to the copolymer; natural rubber; or a synthetic rubber such as for instance a polybutadiene, styrene-butadiene or acrylonitrile-butadiene rubber. A thermoplastic resin material can be non-crystalline (as in amorphous polystyrene) or crystalline (as in crystalline polyethylene or polypropylene). Other types of synthetic materials that can be employed include polyamides, such as for example nylon 11 and nylon 66; polyurethanes, polylactams, such as a polycaprolactam; and polyesters, such as of the poly-

ethylene terephthalate type. Where the thermoplastic material is regenerated natural fibre it is preferably one based on cellulose, for example rayon, cellulose acetate, cellulose triacetate or cellulose acetate-butyrate.

In the process of the invention the starting material is an extruded foamed polymeric material, and if desired this can be produced by conventional extrusion techniques. The extruded foamed products of British Patent Specification Nos. 22745/64 (Serial No. 1089562) and 28280/64 (Serial No. 1089561) can also be employed. Where an extruded foamed sheet or board is employed this can vary in width through a broad range, but normally it will be at least 3 or 4 cells "thick", and probably there will be at least 10 cells measured through the thickness of a sheet. In practice the thickness can for instance be between 0.05 and 2 inches, for instance between 0.1 and 1 inch. A useful range is often from 0.2 to 0.5 inch. The density of the foamed material can for instance be between 1 pound and 10 pounds or more per cubic foot, such as from about 2 to 4 or 5 pounds per cubic foot. The fact that a starting material is foamed can also be expressed in terms of the volume fraction of voids that it contains, and this can be as low as 0.5. However, in practice the volume fraction of voids is often not less than 0.9, so that the range can for instance be from 0.95 to 0.985, for instance from 0.96 or 0.97 to 0.98. A volume fraction of voids of 0.5 corresponds to a ratio of the volume of foam over the volume of thermoplastic material it contains of two to one.

In general in the production of the extruded foamed thermoplastic material the blowing agent will be a low boiling substance or a chemical blowing agent. The foamed material usually contains closed cells, although material (for instance polyethylene) can be employed which contains cells which to some extent are interconnecting or "open". In many instances the agent is a volatile substance, and is often one that is a gas or vapour under normal atmospheric conditions (such as 20°C. and 1 atmosphere pressure), but which while under presssure before extrusion will be present in solution in the molten or semi-molten thermoplastic material. The blowing agent can however be one, such as pentane or a pentane fraction, which is a volatile liquid under normal conditions. Examples of volatile substances that can be used include lower aliphatic hydrocarbons, such as methane, ethane, ethylene, propane, a butane, or a pentane; low alkyl halides, such as methyl chloride, trichloromethane or 1,2-dichlorotetrafluoroethane; acetone; and inorganic gases, such as carbon dioxide or nitrogen. The lower aliphatic hydrocarbons, especially butane, are useful in respect of polyolefinic materials, such as polystyrene and polyethylene. The blowing agent can also be a chemical blowing agent, which can for example be a bicarbonate such as for example sodium bicarbonate or ammonium bicarbonate, or an organic nitrogen compound that yields nitrogen on heating, such as for example dinitrosopentamethylenediamine or barium azodicarboxylate. From 3 to 30%, especially 7 to 20%, by weight based on the weight of the thermoplastic material is often a suitable proportion of blowing agent, and for example the use of from 7 to 15% by weight of butane in conjunction with a polyolefinic material has given excellent results. Sometimes the blowing agent will be employed in conjunction with a nucleating agent, which assists in the formation of a large number of small cells. A wide range of nucleatting agents can be employed, including finely-divided inert solids such as for example silica or alumina, perhaps in conjunction with zinc stearate, or small quantities of a substance that decomposes at the extrusion temperature to give a gas can be used. An example of the latter class of nucleating agents is sodium bicarbonate, used if desired in conjunction with a weak acid such as for example tartaric acid or citric acid. A small proportion of the nucleating agent, for example up to 5% by weight of the thermoplastic material, is usually effective. A plasticiser can also be present where this is appropriate.

The extruded foamed resin can be used in the form of a sheet or board, in which case it will often have been made using a slit die; sheet material can also be produced using an annular die by extrusion of a tube of foamed material, which can either be slit longitudinally and opened out into a sheet or collapsed so as to form a sheet of double thickness.

The extruded foamed thermoplastic material is drawn, and in doing so it is orientated unidirectionally and the cells of the foam are elongated. In practice it is convenient to draw the foam along the direction in which it has been extruded (that is to say it is drawn uniaxially), but if desired appropriate arrangements can be made for the foamed material to be drawn in a direction for example at right angles to the direction of extrusion. The drawn material usually has a slightly higher density than the material before drawing.

The precise conditions that are necesssary in the drawing operation to achieve the required results depend on the particular thermoplastics material that is employed, but in general draw-down ratios of from 20:1 to 2:1 have been found useful, for example from 15:1 to 3:1. Good results have been obtained with a ratio between 12:1 and 5:1, for instance from 10:1 to 7:1. The temperature employed again depends on the

particular thermoplastic material, but it is an elevated one in most instances, for example above 40°C. or 50°C. and up to 130°C. or 140°C. or rather more in some cases. A temperature in the range of 80°C. to 100°C., such as about 90°C., is often useful. In principle it is desirable for the foamed material to be heated to a moderately elevated temperature, not high enough to damage the foam structure but high enough for the material to be sufficiently ductile. For instance, extruded foamed polystyrene can be drawn at from 120°C. to 140°C., while for foamed high density polyethylene a temperature between 40°C. and 100°C. is preferable. An amorphous thermoplastic material should normally be drawn above its glass transition temperature, whilst a crystalline thermoplastic material can be drawn at a temperature lower than its crystalline melting point. If the foamed material is still hot from the extrusion operation it may need to be cooled before it is possible to draw it in a subsequent operation, but in the more normal course of events a foamed material needs to be heated to a suitable temperature before it can be drawn, because for example even in a continuous operation the temperature of the foamed material can have dropped too low by the time it is possible to draw it. The heat treatment that is applied is as has been explained such that the extruded foam is sufficiently ductile to be drawn, and this can involve for instance either heating the foamed material at a steady temperature, or subjecting it to a relatively high temperature (perhaps as high as 200°C.) for a short time followed by a period (normally longer) at a lower temperature. For example a foamed material that is produced in a form which has an outer "skin" of material (which has a higher density than the inner material) may give better results with a heat treatment which involves a short initial period at a higher temperature. This initial treatment can be useful in the instance of a thermoplastic material such as crystalline polypropylene, and can be as short as a few seconds. The precise conditions necessary in order to ensure that a foamed material is in a condition suitable for drawing can easily be found by simple experiments.

In general any convenient method of applying heat can be employed. For example the extruded foamed material can be passed though hot air or some inert gas, or though a heated bath of a suitable inert liquid, such as water, glycerol or ethylene glycol. In certain instances the drawing can be performed at room temperatures, for example with nylon materials.

After the foamed material has been drawn it is fibrillated by the action of the turbulent stream of fluid. It is often found desirable to subject the drawn material before it is fibrillated to some form of working so that some shear is applied to it, preferably in a transverse direction, and several ways of doing this can be employed, including rubbing, rolling, twisting, shaking or beating. For example the drawn material can be mechanically worked by passsing it through the nip between a series of reciprocating rollers or between reciprocating bars. In a preferred process according to the invention, however, this working is accomplished by the action of a jet of fluid (which can be turbulent or streamline) directed on to the surface of the thermoplastic material, and the fluid can then subsequently form the turbulent stream that accomplishes fibrillation. A preferred process according to the invention comprises the steps of supporting the drawn material, for example within a tube, and directing on to it a jet of fluid (which can be streamline or turbulent) in a direction at an angle to the direction of orientation of the drawn thermoplastic material, the fluid subsequently forming a turbulent stream which completes the fibrillation. There can be several such jets arranged around the circumference of the tube, or the jet can be annular. An example of an apparatus producing an annular jet is described below. The angle at which a jet of fluid strikes the drawn material is dependent on the design of the apparatus and the degree of turbulence required, which in turn depends on the type of product desired. As a general rule angles up to 180 degrees to the direction of orientation of the thermoplastic material have been found to be effective, and particularly between 60 and 120 degrees, for example 80—100 degrees Where the material is itself moving the jet can have a component of motion parallel to or contrary to the material's direction of movement.

Where the drawn foamed material is supported within a tube this need not have a solid wall, for example it can be perforated or made of porous material or even of wire gauze. Preferably however the walls of the tube are solid apart from one or more holes to allow for the entry or exit of the fluid, since then the passage of the fluid through the tube creates greater turbulence and thus more effective fibrillation. The cross-sectional area of the tube is preferably from 1 to 5 times, for example about twice, that of the unfibrillated strand.

Two examples of a suitable apparatus for performing the process of the invention will now be described with reference to the accompanying Drawings, in which:

Figure 1 shows a side elevation of one apparatus partly in section; and

Figure 2 shows a side elevation, partly in section, of a second apparatus, which employs an annular jet.

The apparatus shown in Figure 1 comprises a tube (1) through which a strand

passed, having a narow section (2) leading into a fibrillation chamber (3) which comprises a section of wider and diverging bore provided with a slit jet (4). At the exit, the walls of the fibrillation chamber widen out forming a trumpet-shaped outlet (5). The slit jet (4) is connected via a pipe (6) to a source (not shown) of fluid, for example compressed air.

In operation, a strand of drawn foamed thermoplastic material is fed into the tube (1), passes through the narrow section (2) and is struck at an angle by a jet of fluid from the slit jet (4). The strand is partially broken down by the initial impact of the jet of fluid upon it, and the fibrillation process is continued by the action of the resulting turbulent stream within the fibrillation chamber (3). Both the fibrillated strand and the spent fluid leave the fibrillation chamber by the trumpet-shaped outlet (5).

The apparatus shown in Figure 2 similarly comprises a tube (11) having extending into it from one end a hollow nozzle (12) through which a strand of the drawn thermoplastic material can be passed. Surrounding the nozzle (12) is a space (13) of annular cross-section that has communicating with it a pipe (14) leading to a source (not shown) of fluid, for example compressed air. The nozzle (12) is externally tapered at its end (15), adjacent to which is a plate (16) extending across the tube and having at its centre a tapered orifice (17) so that there is defined between the nozzle end (15) and the sides of the orifice (17) an annular jet (18). Downstream of the jet the tube (1) narrows at (19) and opens out again to a trumpet-shaped outlet (20) so as to form a venturi section. The position of the venturi section, and hence the annular width of the jet (18), can be adjusted by means of the knurled wheel (21).

The action of the fluid on the strand is such that the strand is conveyed through the tube at a speed depending upon the fluid speeds. Where the fluid is air, for example, strand speeds of up to 300 feet per minute, for example from 100 to 200 feet per minute, are generally suitable. No external feeding or pulling of the strand through the tube is normally required, and in some cases such feeding or pulling has been found to be disadvantageous since it can interfere with vibration and consequent fibrillation of the strand.

Other forms of apparatus for carrying out the process of the invention can for example comprise a pair of pulleys which carry a strand or other elongated piece of the drawn thermoplastic material and a jet disposed so as to direct a turbulent stream of fluid on to the material as it passes between the pulleys. With this system it has sometimes been found difficult to keep the strand located within the fluid stream, and in some circumstances it may be preferable to support the material, particularly where it is in a form wire than a strand, on for example a gauze covered drum or in a U-shaped gauze channel, while the fluid stream is directed on to it. Alternatively the fluid stream can be directed against the material as the latter passes over a V-pulley. By adjusting the turbulent stream of fluid to strike the sides of the V-pulley it has been found that the fibrillated material can be given a superficial coating of the fine broken fibrils similar to those of a woollen yarn.

The invention will now be illustrated by the following Examples.

Example 1

This Example describes the production of a fibrillated strand of polypropylene using a process according to the invention.

An appartus similar to that shown in Figure 1 of the accompanying Drawings was used in which the section (2) had a diameter of 2—3 millimetres, the chamber (3) had a diameter of about 8 millimetres at its mid-point and the slit nozzle had dimensions 5 millimetres by 0.8 millimetres. A strand of drawn foamed polypropylene having a diameter of 2 millimetres and a draw-down ratio of 7 was blown through the tube at a speed of 50 feet per minute by means of air at a pressure of 70 pounds per square inch forced through the slit nozzle at the rate of 90 litres per minute, and there was produced a strand of fibrillated polypropylene having a soft silky texture and a tensile strength of 1.9 grams per denier.

Example 2

This Example describes the production of a fibrillated strand of polyethylene employing an annular jet of air in a process according to the invention.

A strand of drawn foamed polyethylene having a diameter of 2 millimetres and a draw-down ratio of 10:1 was passed through an apparatus as shown in Figure 2 of the accompanying Drawings. The diameter of the orifice (17) at its narrowest part was 0.15 inch and the diameter of the nozzle (12) at its end (15) was 0.125 inch, and the width of the annular jet was set at 0.015 inch. The narrow portion (19) of the venture section was situated 0.35 inch down stream from the plate (16) and was 0.1 inch in diameter. The trumpet-shaped outlet was 0.2 inch in diameter at its widest poit, which was 1.3 inch down stream from the narrow portion (19).

The drawn foamed strand was blown through the apparatus at a speed of 700 feet per minute by means of air at a pressure of 60 pounds per square inch forced through the annular jet at the rate of 200

litres per minute reduced to normal temperature and pressure.

The resulting strand was particularly evenly and finely fibrilated, the fibre elements it contained being well spaced laterally from one another. It has a very soft silky texture and a tensile strength of 3.0 grams per denier.

WHAT WE CLAIM IS:—

1. A process for the production of a fibrous material, which comprises drawing an extruded foamed thermoplastic material so that it becomes orientated essentially in one direction, and subjecting the drawn foamed material to the action of a turbulent stream of fluid so that the walls of the foam are broken down and converted into a fibrous material.

2. A process according to Claim 1, in which the drawn thermoplastic material is caused to vibrate at an audio frequency within the stream of fluid so that fibrillation occurs.

3. A process according to either of Claims 1 and 2, in which the speed of the fluid stream is subsonic.

4. A process according to Claim 3, in which the speed is not greater than 20 feet per second.

5. A processs according to any of the preceding claims, in which the fluid is a gas.

6. A process according to Claim 5, in which the gas is air.

7. A process according to any of the preceding claims, in which the extruded foamed thermoplastic material is a strand or ribbon and there is produced a textile yarn.

8. A process according to any of the preceding claims, in which the thermoplastic material is a polymer or copolymer of an ethylenically unsaturated hydrocarbon.

9. A process according to Claim 8, in which the hydrocarbon is ethylene or propylene.

10. A process according to any of the preceding claims, in which the drawn material is subjected before it is fibrillated to working so that shear is applied to it in a transverse direction.

11. A process according to Claim 10, in which the working is accomplished by the action of a jet of fluid directed on to the surface of the thermoplastic material.

12. A process according to Claim 11, in which the jet of fluid subsequently forms the turbulent stream that accomplishes fibrillation.

13. A process according to Claim 12, which comprises supporting the drawn material and directing on to it a jet of fluid in a direction at an angle to the direction of orientation of the drawn thermoplastic material, the fluid subsequently forming a turbulent stream which completes the fibrillation.

14. A process according to Claim 13, in which the angle between the direction of a jet and the direction of orientation of the drawn material is between 60 and 120°.

15. A process according to either of Claims 13 and 14, in which the drawn material is supported within a tube.

16. A process according to Claim 15, in which there is employed an apparatus substantially as hereinbefore described with reference to and as illustrated in Figure 1 of the accompanying Drawings.

17. A process for the production of a fibrous material substantially as described in Example 1.

18. A process according to any of Claims 13 to 15, in which there is employed an annular jet of fluid.

19. A process according to Claim 18, in which there is employed an apparatus substantially as hereinbefore described with reference to and as illustrated in Figure 2 of the accompanying Drawings.

20. A process for the production of a fibrous material substantialy as described in Example 2.

21. A fibrous material that has been produced by a process according to any one of Claims 1 to 17.

22. A fibrous material that has been produced by a process according to any of Claims 18 to 20.

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1157695 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

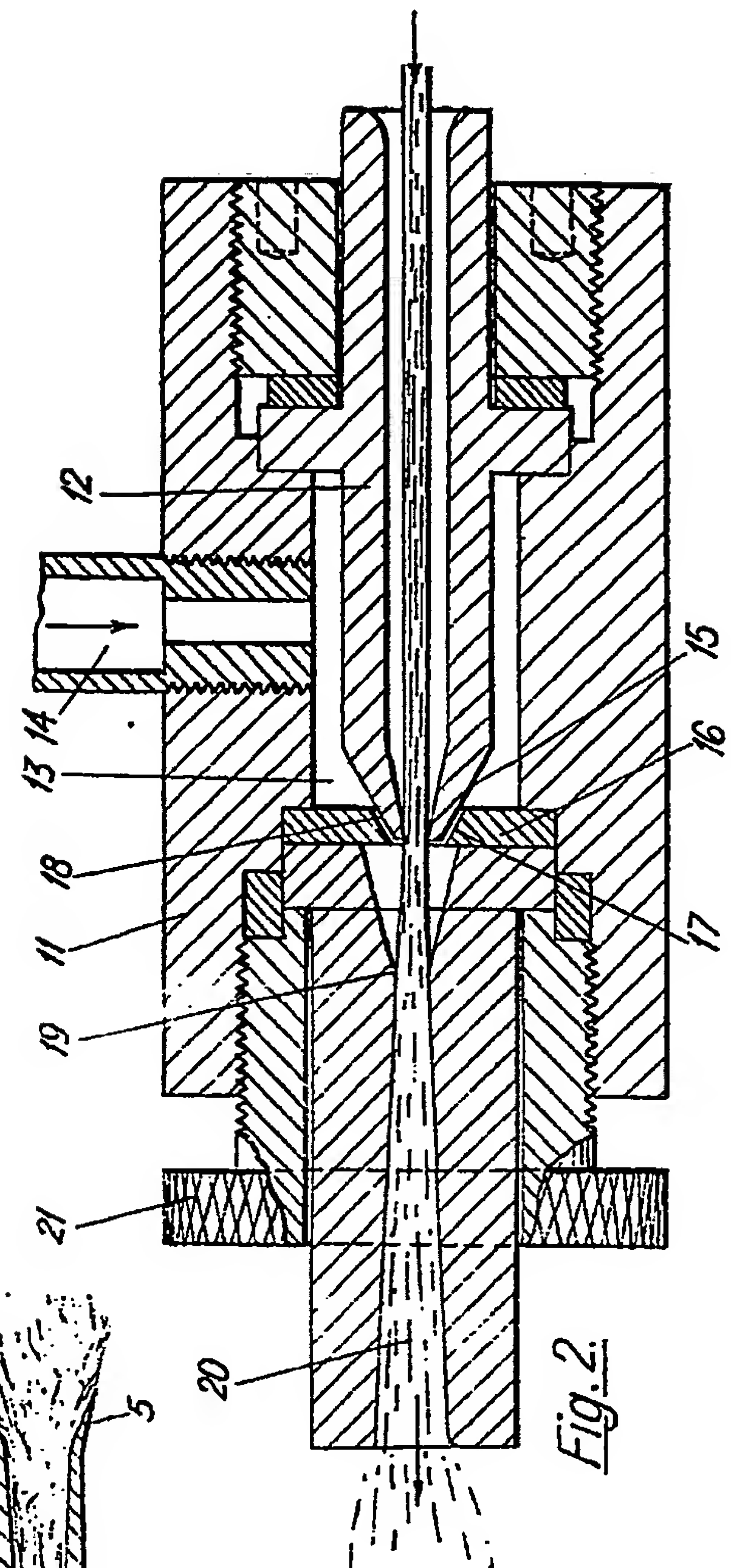

Fig.2

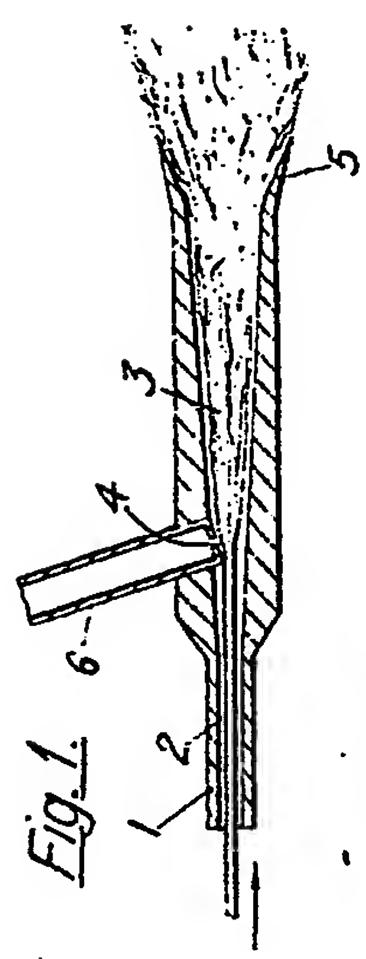

Fig.1